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Theoretical Studies of Photochemical Methods for
Semiconductor Etching

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The general theme of the project is the use of photochemical methods for
etching semiconductor surfaces or depositing metals on them. There are
two aspects to this work: (a) the photochemical process by which the
desired molecular or atomic fragments are deposited on the surfaces and
(b) the fate of the atoms once deposited (e.g. motion of the atoms on
the surface, island growth, sticking probabilities, etc.)

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Surface diffusion, time-dependent, quantum mechanics,
photodissociation, surface reaction rater

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1. Brief Description of the Project

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Our work covers selected topics in both areas. We have developed new quantum methods for calculating the dynamics of photo-decomposition and the rate of migration of adsorbed atoms.

2. Significant Results.

(a) *Photodissociation.*We have developed extremely efficient methods for calculating various observables pertinent to phctodissociation: the velocity and the angular distribution of the fragments and the spectroscopic quantities which serve as an indirect probe of photodissociation dynamics. The methodology has been used to study photodissociation induced by very strong laser fields and ultra-short pulses, or the results of time independent, steady state experiments.

This work is at the leading edge of a program (involving few other groups) whose purpose is to add a new intellectual dimension to the theory of photodissociation and spectroscopy, by optimizing substantially the way we compute and by changing the way we think about the results. We do this by breaking away from the long standing tradition stipulating that, to calculate you must find the eigenstates of the total Hamiltonian and to interpret, you must catalog the relevant overlap integrals. We go back to the time dependent formulation of spectroscopy and compute observables by solving directly the time dependent Schrodinger equation. This can be done extremely efficiently by using spectral methods developed in the past ten years in fluid dynamics and electrodynamics. Conceptually, the time dependent formulation places time and nuclear motion at the heart of spectroscopy: spectra are now connected to the way the nuclei move after or during the excitation.

This theory can be applied to any kind of spectroscopy, but it is especially advantageous in studying steady state photodissociation, the

break up of molecules excited by ultra-short pulses or the effect of very strong laser fields.

Two of our early papers extended the methodology for solving the time dependent Schrodinger equation to include extended wave functions[1] and curve-crossing systems.[2] The method developed in ref. [1] was used to do the first calculation of the atomic relative energy distribution following the dissociation of a diatomic by an extremely strong laser. The absorption and the Raman spectra of a model system were studied in the papers [12] and [17]. These are the first time dependent calculations of such spectra, for two-dimensional systems involving curve crossing. They were based on the method developed in paper [2]. Finally, in paper [14] we were the first to introduce a time dependent method for calculating Moller operators, which can be used to calculate final state energy distribution after dissociation. We applied the method to calculate the initial energy dependence of photon induced recombination of two colliding hydrogen atoms.
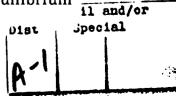
All these calculations represent new applications of the time dependent methodology and their purpose was to develop the computational strategy and the physical interpretation. The examples were chosen to illustrate the power of the methodology.

In the papers [21,22,24] our aim was to provide a complete interpretation of very recent "femtochemistry" experiments of Zewail, and to predict how the results depend on experimental conditions not yet used in the laboratory. These experiments have received an extraordinary amount of attention from theorists and our work is, so far, the most thorough and definitive.

(b) Reaction rates in surface science quantum systems. Our main effort has been directed towards the development of new methods for computing thermal rates in quantum systems, which-we believe-will be substantially better than those used before. We have applied them to hydrogen diffusion on metals, but they are applicable to all reactions in which the reaction coordinate, and few other degrees of freedom, are quantum mechanical and the medium can be treated classically. The rate constant calculations use the quantum correlation function formulation introduced by Yamamoto, in the form given by W.H. Miller. Our early efforts were directed towards the development of efficient methods for calculating quantum correlation functions: we showed how a fast Fourier transform method can be used to calculate extremely efficiently the flux-flux correlation function[3] and thermal equilibrium

properties[4]. The correlation function method was extended to give the rate coefficient for systems with more than one electronic state[9].

This methodology was used to study hydrogen motion on Cu(100). Besides providing accurate model calculation we have also clarified a number of important physical questions: (α) the role of hydrogen motion perpendicular to the surface[13,19]; (β) the mechanism for randomizing parallel momentum[19] (χ) the role of multiple jumps[11,19]. A major effort has been and is currently devoted to the development of more rigorous and computationally better versions of quantum transition state theory[25].

Because it is based on large scale computer simulations the methodology developed in our work has wide applicability. It can be used for calculations of rate coefficients in all quantum systems (e.g. proton, hydrogen atom or electron transfer reactions), in condensed media (liquids, protein, solids, surfaces) or in gas phase. It also provides a logically rigorous and computationally advantageous transition state theory for quantum systems. Furthermore, the method for computing correlation functions can be applied to other phenomena (such as light absorption, Raman line shapes or conductivity) for which the observable of interest can be written as a correlation function.

Other work in the area of kinetic processes at surfaces was concerned with improved efficiency of classical simulations of surface atom dynamics[18] and its application to study the damage induced by hyperthermal (low energy E< 30 eV) atomic beams[19]. Finally, in paper [2] we reported the first fully quantum mechanical, two dimensional study of H_2 dissociation on a Ni surface. Such studies are useful for assessing the importance of the quantum effects and providing some qualitative insights regarding the factors controlling reaction dynamics. In paper [5] we studied the effect of phase transitions on diffusion measurements using laser induced desorption. This is a very interesting area of research, which we have abandoned due to insufficient personnel.

Finally, we published two papers regarding luminescence and two photon photochemistry at a metal surface. This work was supported by our previous ONR contract and was published with some delay.

3. Awards and Honors

During the tenure of this grant the principal investigator has been elected:

- Fellow of the American Physical Society
- Research Faculty Lecturer at the University of Californa at Santa Barbara (the highest campus honor for a senior faculty member).
- Vice-chairman (for 1991) and Chairman (for 1993) of the Gordon Conference on "Dynamics of Gas Surface Interactions".
- Organized ACS Meeting 1987

4. The reception of the work

This work was very well received. We were invited to present it at international meetings, National ACS and APS meetings, Gordon conferences and in leading chemistry departments.

1987

Seminar, Time Dependent Quantum Processes, California Institute of Technology, Chemistry Department, January.

Seminar, Time Dependent Quantum Processes, University of Nebraska, Department of Chemistry, January.

Invited Speaker, Time Dependent Theory of Surface Science Processes, Kendall Symposium, American Chemical Society National Meeting, Denver, CO, April.

Invited Speaker, Time Dependent Processes at Surfaces, 1987 Conference on Dynamics of Molecular Collisions, WV, July.

Invited Speaker, Workshop on Electromagnetic Response of Surfaces, Taxco, Mexico, August.

Invited Speaker, Time Dependent Quantum Processes, The American Conference on Theoretical Chemistry, Gull Lake, MN, July.

Invited Speaker, Dynamic Processes at Surfaces, Symposium on Surface Dynamics, American Chemical Society National Meeting, New Orleans, LA, September.

Seminar, Penning Ionization As a Probe of Adsorbed Molecules, Department of Chemistry, University of California, Riverside, October.

Seminar, Time Dependent Methods in Quantum Dynamics, Department of Chemistry, University of Chicago, IL, November.

Seminar, Time Dependent Methods in Quantum Dynamics, Department of Chemistry, Northwestern University, IN, November.

Seminar, Time Dependent Methods in Quantum Dynamics, Department of Chemistry, University of Pittsburgh, PA, December.

1988

Seminar, Time Dependent Methods In Quantum Dynamics, Department of Chemistry, University of Colorado, February.

Invited Speaker, Time Dependent Methods for Calculating Molecule Surface Dynamics, American Physical Society Meeting, Symposium on New Computational Methods, New Orleans, LA, March.

Lecturer, Surface Molecule Collisions, International Theoretical Physics School, Institute of Theoretical Physics, Trieste, Italy, May.

Seminar, Department of Chemistry, Time Dependent Quantum Methods, University of Toronto, May.

Invited Speaker, Quantum Rates By Time Dependent Methods, Satellite Meeting on Chemical Reaction Dynamics, Jerusalem, Israel, August.

Invited Speaker, Thermal Rate Theory: Surface Diffusion, Gordon Conference on Atomic and Molecular Interactions, Plymouth, NH, August 1-5.

Invited Speaker, Hydrogen Diffusion on Surfaces, Surface Science Symposium, American Chemical Society National Meeting, Los Angeles, CA, September.

Seminar, Hydrogen Diffusion, Department of Chemistry, University of Washington, November.

1989

Seminar, Electron Scattering by Adsorbed Molecules, Physics Department, University of Texas at Austin, January.

Seminar, Time Dependent Quantum Theory of Photodissociation, Department of Chemistry, University of Colorado, Boulder, February.

Seminar, Time Dependent Quantum Dynamics in Photochemistry, Department of Chemistry, University of Maryland, March.

Invited Speaker, Symposium on Solid State Dynamics, Hydrogen Diffusion on Surfaces, American Chemical Society National Meeting, Dallas, TX, April 9-14.

Invited Speaker, International Workshop on Surface Molecule Dynamics, Copenhagen, May.

Invited speaker, Hydrogen Diffusion on Surfaces, Conference on Quantum Monte Carlo, Los Alamos, July.

Invited Speaker, Hydrogen Diffusion of Surfaces, Gordon Research Conference on Molecule Surface Interactions, August, 1989.

Seminar, Time Dependent Quantum Theory of Photodissociation

1990

Department of Chemistry, Stanford University, November 9, 1989

Seminar, Hydrogen Diffusion on Surfaces, Department of Chemistry, University of Houston, February, 1990.

Seminar, Chemistry Department, University of Texas, Austin, February, 1990.

Invited Speaker, Symposium on Classical and Quantal Simulations, ACS National Meeting, Boston, April 23-27, 1990

Invited Speaker, Symposium on Molecular Dynamics, ACS National Meeting, Boston, April 23-27, 1990.

5. Publications supported by ONR

1. An Efficient Procedure for Calculating the Evolution of the Wave Function by Fast Fourier Transform Methods for Systems With Spatially Extended Wave Function and Localized Potential, R. Heather and H. Metiu, J. Chem. Phys. $\underline{86}$, 5009 (1987).

2. The Dynamics of H_2 Dissociation on Ni(100): A Quantum Mechanical Study of a Restricted Two-Dimensional Model, B. Jackson and H. Metiu, J. Chem. Phys. $\underline{86}$, 1026 (1987).

3. A Time Dependent Method For Computing Thermal Rates Constants, G. Wahnström and H. Metiu, Chem. Phys. Lett. $\underline{134}$, 531 (1987).

4. An Efficient Monte Carlo Method for Calculating the Equilibrium Properties For a Quantum System Coupled Strongly to a Classical One, B. Carmeli and H. Metiu, Chem. Phys. Lett. $\underline{133}$, 543 (1987).

5. A Monte-Carlo Analysis of Diffusion Measurements In Surface Science Systems That Undergo Phase Transitions, X-P. Jiang, H. Metiu, J. Chem. Phys. $\underline{88}$, 1891 (1988).

6.   A Numerical Study of the Correlation Function Expressions for the Thermal Rate Coefficients in Quantum Systems, G. Wahnström and H. Metiu, J. Phys. Chem. 92, 3241 (1988).

7.   Multiphoton Dissociation of a Diatomic Molecule: Laser Intensity, Frequency and Pulse Shape Dependence of the Fragment Momentum Distribution, R. Heather and H. Metiu, J. Chem. Phys. 88, 5496 (1988).

8.   The Evolution of the Wave Function in a Curve Crossing Problem Computed by a Fast Fourier Transform Method, J. Alvarellos and H. Metiu, J. Chem. Phys. 88, 4957 (1988).

9.   An Exact Theory for the Thermal Rate Coefficient in a Curve Crossing System, R. Almeida and H. Metiu, Chem. Phys Lett. 146, 47 (1988)

10.   The Calculation of the Thermal Rate Coefficient by a Method Combining Classical and Quantum Mechanics, G. Wahnström, B. Carmeli and H. Metiu, J. Chem. Phys. 88, 2478 (1988).

11.   Multiple Jump Rates for Site-to-Site Hopping on a One-Dimensional Lattice, G. Wahnström and H. Metiu, Chem. Phys. Lett. 145, 44 (1988).

12.   The Use of Raman Spectroscopy to Study Photodissociation Dynamics for Systems Where Curve Crossing is Important, R. Heather, X-P. Jiang and H. Metiu, Chem. Phys. Lett. 142, 303 (1987).

13.   A Model Study of Hydrogen Diffusion on Surfaces: Barrier Recrossing, Multiple Jumps and Randomization, G. Wahnström, K. Haug and H. Metiu, Chem. Phys. Lett. 148, 158 (1988).

14.   The Relative Kinetic Energy Distribution of the Hydrogen Atoms Formed by the Dissociation of the Electronically Excited H_2 Molecule, V. Engel and H. Metiu, J. Chem. Phys. 89, 1986 (1988).

15.   A Study of Fluorescent Intensity Emitted by Eu^{3+} Ions Near Dielectric Interfaces, Q.Q. Shu, P.K. Hansma, P. Das and H. Metiu, J. Luminescence 40&41, 745 (1988).

16. Surface Enhanced Two Photon Absorption Near a Small Metal Particle, P.C. Das, H. Metiu and A. Puri, J. Chem. Phys. 89, 6497 (1988).

17. Time Dependent Calculations of the Absorption Spectrum of a Photodissociating System with Two Interacting Excited Electronic States, X-P. Jiang, R. Heather and H. Metiu, J. Chem. Phys.,90,2555(1989)

18. Molecular Dynamics Simulations of Energy Flow at a Solid Surface: New Methods Using a Small Number of Atoms, A.E. DePristo and H. Metiu, J. Chem. Phys. 90, 1229 (1989).

19. Hydrogen Motion on a Cu Surface: A Model Study of the Rate of Single and Double Site-to-Site Jumps and the Role of the Motion Perpendicular to the Surface, K. Haug, G. Wahnström and H. Metiu, J. Chem. Phys. 90, 540 (1989).

20. Molecular State Evolution After Excitation with an Ultra-Short Laser Pulse: An Exact Quantum Analysis of NaI and NaBr Dissociation, V. Engel, H. Metiu, R. Almeida, R.A. Marcus and A.H. Zewail, Chem. Phys. Lett. 152, 1 (1988).

21. The Study of NaI Predissociation with Pump-Probe Femtosecond Laser Pulses: The Use of an Ionizing Probe Pulse to Obtain More Detailed Dynamic Information, V. Engel and H. Metiu, Chem. Phys. Lett. 155, 77 (1989).

22. Surface Damage Caused by Bombardment with Low Energy (10-30 eV) Argon, H. Metiu and A.E. DePristo, J. Chem. Phys.,90, 2735, (1989).

23. The Time Dependent Theory of Raman Scattering for Systems with Several Excited Electronic States: Application to an H_3^+ Model System, R. Heather and H. Metiu, J. Chem. Phys. 90, 6903, (1989).

24. A Quantum Mechanical Study of Predissociation Dynamics of NaI Excited by a Femtosecond Laser Pulse, V. Engel and H. Metiu, J. Chem. Phys. 90, 6116, (1989).

25.   Hydrogen Motion on a Rigid Cu Surface: The Calculation of the Site to Site Hopping Rate by Using Flux-Flux Correlation Functions, K. Haug, G. Wahnström and H. Metiu, J. Chem. Phys. (accepted).

6. Personnel

Dr. Horia Metiu
Dr. Robert Heather
Dr. Volker Engel
Dr. Xue-Pei Jiang
Dr. Lit-Neh Chang